

Pyraclostrobin

Summary of Analytical Chemistry and Residue Data

DP#: 380634

**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460****MEMORANDUM**

**OFFICE OF CHEMICAL SAFETY AND
POLLUTION PREVENTION**
OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

Date: 03/16/2011**SUBJECT: Pyraclostrobin:** Section 3 Registration of a New Microencapsulated Product BAS 500 20F (EPA Reg. No. 7969-GRU) for Use on Corn (Field, Pop and Seed Production).**PC Code:** 099100**Decision No.:** 432361**Petition No.:** N/A**Risk Assessment Type:** N/A**TXR No.:** N/A**MRID Nos.:** 48037306 & 48037315**DP Barcode:** D380634**Registration No.:** 7969-GRU**Regulatory Action:** Section 3 Registration**Case No.:** N/A**CAS No.:** 175013-18-0**40 CFR:** 180.582

Ver. Apr. 08

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Rec'd in RAC
3/17/2011
EL

I. CONCLUSIONS

HED has no objection granting registration for BAS 500 20F (EPA Reg. No. 7969-GRU), a 2 lbs ai/gal formulation, for use on corn (field, pop and seed production corn). The proposed new formulation use is not likely to result in residues exceeding the permanent tolerance levels established in 40 CFR §180.582(a) for these crops (ChemSAC minutes, 2/16/2011).

II. ACTION REQUESTED

BASF Corporation (BASF) has requested registration of a new aqueous capsule suspension product BAS 500 20F containing pyraclostrobin at 2 lb ai/gal for use on corn including field corn, pop corn and seed production corn.

III. BACKGROUND

Formulation

BASF currently has two pyraclostrobin end-use products (EPs), Headline® Fungicide (EPA Reg. No. 7969-186) and Headline® Fungicide SC (EPA Reg. No. 7969-289), that are registered for use on corn. These EPs are 2 lb ai/gal emulsifiable concentrate (EC) and suspension concentrate (SC) formulations, respectively. The new formulation, BAS 500 20F, is an aqueous capsule suspension product containing pyraclostrobin at 2 lb ai/gal.

Tolerances

There are established tolerances for residues of pyraclostrobin in/on corn commodities ranging from 0.04-23 ppm: 0.1 ppm on corn, field, grain and corn, pop, grain; 5 ppm on corn, field, forage and corn, sweet, forage; 17 ppm on corn, field, stover and corn, pop, stover; 23 ppm on corn, sweet, stover; and 0.04 on corn, sweet, kernel plus cob with husk removed; and 0.2 ppm on corn, field, refined oil [40 CFR §180.582(a)(1)].

Directions for Use

Currently, pyraclostrobin may be foliar-applied to corn at a maximum seasonal rate of 1.2 lb ai/A (0.2 lb ai/A/application) and a pre-harvest interval (PHI) of 7 days.

A summary of the registered/proposed pyraclostrobin crop use patterns for use on corn is presented in Table 1.

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TABLE 1. Summary of Registered/Proposed Use of Pyraclostrobin.						
Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A) fl oz/A	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A) fl oz/A	PHI (days)	Use Directions and Limitations
Corn including field corn, pop corn, sweet corn, seed production corn (Registered Use)						
Broadcast foliar spray; Ground or aerial	Headline® Fungicide [EPA Reg. No. 7969-186]/ Headline® SC Fungicide [EPA Reg. No. 7969-289]	(0.10-0.20) 6-12	NS	(1.18) 72	7	Applications may begin prior to disease development and continue on a 7- to 14-day interval. Use higher rate (0.15-0.2 lb ai/A, 9-12 fl oz/A) when disease pressure is high (Northern leaf blight and Southern leaf blight). The use rate in California is 9-12 fl oz/A. The maximum product rate per season included the combination of in furrow and foliar uses. The product may be used with adjuvants. Resistance Management: To limit the potential for development of resistance, do not apply more than 1.18 lbs ai/A (=72 fl oz/A/season). In field corn, do not make more than two applications per season. Do not make more than 2 sequential applications before alternating to a labeled non-group 11 fungicide with a different mode of action.
Corn including field corn, pop corn, seed production corn (Proposed)						
Ground; aerial; sprinkler irrigation equipment.	BAS 500 20F Aqueous Capsule Suspension [7969-GRU]	(0.1) 6 fl ozs/A	1	(0.1) 6 fl ozs/A	7	Begin applications prior to disease development. May be used with adjuvants. No livestock feeding restrictions. One additional application of pyraclostrobin-containing product may be made at the VT stage of growth or later, delivering up to 0.2 lb ai/A pyraclostrobin. Do not exceed a total of 0.3 lb ai/A for the combined use of pyraclostrobin-containing products in field corn or seed corn when BAS 500 20F is included in the treatment program.

Restrictions and Limitations:

The product should not be applied after the V8 growth stage of corn. The label states that crops listed on BAS 500 20F, Headline fungicide, Cabrio fungicide and Pristine fungicide labels maybe planted immediately following the last application. For all other crops, do not plant sooner than 14 days after the last application.

General application information on the label states that the product should not be used in greenhouse or transplant production. For optimum results in cases of high disease pressure, the label recommends use of a minimum spray volume of 4 gallons per acre (GPA). For aerial applications, 2 or more gallons of spray solution per acre is recommended. No aerial application is allowed in New York State. The product should be applied only through sprinkler irrigation systems (center pivot, lateral move, end tow, side (wheel roll), traveler, big run, solid set, or hand move irrigation systems).

For Directed or Banded Sprays Related to ground applications:

BAS 500 20F may be applied as a directed or banded spray over the rows or plant beds with alleys or row middles left unsprayed. For such uses, reduce the rate of BAS 500 20F in proportion to the area actually sprayed. This adjustment is necessary to prevent applying the product at use rates higher than permitted on the label.

Conclusions: The submitted use directions are adequate to allow evaluation of the residue data relative to the proposed use. The submitted field trial data for field corn forage reflect one application of approximately 0.10 lb ai/A made at the V6-V8 stage. In the submitted field trials, samples of field corn forage were harvested at a ~7-day PHI.

Recommendations:

The ChemSAC recommended that the label for the EPs (Headline- EC and SC formulations) be revised to reflect maximum application rate when using a combination of formulations such as microencapsulated+Headline (this issue is already addressed on the BAS 500 20F label).

IV. DISCUSSION

To support this registration, during a presubmission meeting the Agency requested that BASF submit residue data on field corn forage. In response, BASF has submitted field trial data on field corn conducted at 0.1 lb ai/gal using the microencapsulated formulation BAS 500 18F. The registrant has made some changes in the composition of inerts and is requesting to register the amended product BAS 500 20F. Residue data generated with BAS 500 18F are translatable to BAS 500 20F (ChemSAC minutes, 2/16/2011).

In addition, a wash-off study on the encapsulated formulation was evaluated by Environmental Fate and Effects Division (EFED). The result indicated that BAS 500 20F wash-off from the surface of corn plants with adjuvants resulted in slightly higher (8-12%) versus 7% without an adjuvant (R. Miller, DP# 385629, 02/22/11).

Existing data: The field trials on corn were conducted using 6 ground applications at ~0.20 lb ai/A/application (max seasonal rate of ~1.2 lb ai/A) with PHI of 7 days (L. Cheng, DP# 281042, 07/26/04); for field corn only 2 applications are permitted. Comparing the application rates of the registered products with the proposed formulation, the proposed rate is much lower than the registered rate.

Crop Field Trials

Corn

DER Reference List 48037315.der.doc

BASF has submitted crop field trial data for pyraclostrobin in/on field corn. Four crop trials were conducted, encompassing NAFTA Zones 11 (Idaho, 1- trial), 5 (North Dakota, 2- trials), and 1A (Prince Edward Island, 1- trial) during the 2009 growing season. One treated plot and one untreated control plot were established at each trial site. For each trial, one broadcast foliar application of pyraclostrobin as an encapsulated formulation (BAS 500 18F), was made at a target rate of 0.10 lb ai/A at V6-V8 growth stage. The actual application rate was 0.10-0.11 lb ai/A. All applications were made using ground equipment in 18 to 24.5 gal/A of water. An adjuvant (crop oil concentrate) was added to the spray mixtures for all applications. Single control and duplicate samples were collected at 7, 14, and 21 days after the last application.

Residues of pyraclostrobin and its desmethoxy metabolite (500M07) were quantitated using a liquid chromatography with tandem mass spectroscopy (LC/MS/MS) method, BASF analytical method number D9908 (Version II). The method was adequate for data collection based on acceptable concurrent method recoveries. The limit of quantitation (LOQ) was 0.02 ppm for each analyte and the limit of detection (LOD) was 0.004 ppm for each analyte.

Samples were stored frozen for a maximum of 69 days from sampling to extraction. Stability data are available indicating that both pyraclostrobin and 500M07 are stable in various crops, including wheat grain and straw, for up to 25 months in frozen storage (L. Cheng, DP# 269668, 11/28/01). These data are adequate to support the storage conditions and durations of the field corn forage samples.

There are adequate storage stability data from previous pyraclostrobin petition submissions (L. Cheng, PP#0F6139, DP# 269668, 11/28/01). These data may be translated in the current submission to validate sample storage conditions and durations. Pyraclostrobin residues were found to be reasonably stable over a wide range of commodities under frozen storage conditions for up to 25 months.

Following one broadcast foliar application of pyraclostrobin at a target rate of 0.10 lb ai/A, maximum total residues of pyraclostrobin (pyraclostrobin + 500M07, expressed as parent equivalents) in/on field corn forage were 0.63 ppm at a PHI of 7 days, 0.29 ppm at a PHI of 14 days, and 0.10 ppm at a PHI of 21 days.

Conclusions: The submitted data for corn forage are adequate. The field trial data reflect the use of one foliar application of the encapsulated formulation, made to field corn plants at a target rate of 0.10 lb ai/A made at V6-V8 growth stage. Samples were harvested from treated and untreated plots at PHIs of 7, 14, and 21 days at all trials. An acceptable method was used for the

quantitation of residues of in/on field corn forage. Adequate storage stability data are available to support the storage conditions and durations of the samples. Following one broadcast foliar application of pyraclostrobin at a target rate of 0.10 lb ai/A, maximum total residues of pyraclostrobin in/on field corn forage were 0.63 ppm at a PHI of 7 days, 0.29 ppm at a PHI of 14 days, and 0.10 ppm at a PHI of 21 days.

TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyraclostrobin.									
Commodity	Total Appl. Rate lb ai/A [kg ai/ha]	PHI (days) ¹	Residue Levels (ppm)						
			N	Min.	Max.	HAFT ²	Median (STMdR)	Mean (STMR)	Std. Dev.
Pyraclostrobin									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.15	0.54	0.46	0.29	0.29	0.13
		14	8	<0.0 2	0.23	0.20	0.05	0.08	0.08
		21	8	<0.0 2	0.08	0.07	0.04	0.04	0.02
500M07									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.04	0.09	0.09	0.07	0.07	0.02
		14	8	<0.0 2	0.06	0.05	0.02	0.03	0.01
		21	8	<0.0 2	0.02	0.02	0.02	0.02	0.00
Total ³									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.22	0.63	0.55	0.35	0.36	0.14
		14	8	<0.0 4	0.29	0.25	0.07	0.11	0.09
		21	8	<0.0 4	0.10	0.09	0.06	0.06	0.02

¹ PHI = Pre-harvest interval.

² HAFT = Highest Average Field Trial value.

³ Total residues of pyraclostrobin (pyraclostrobin + 500M07), expressed as parent equivalents.

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References

DP Barcode: D385629

Subject: Data Evaluation on the Wash-off of Encapsulated Pyraclostrobin (BAS 500 F) from Corn Plants.

From: R. Miller

To: N/A

Dated: 2/22/11

MRID: 48037313

DP Barcodes: D281042, D286732, D287729, D288459, D290342, D290343, D290369, D292440, D293088, D293684, D295893, and D298178

Subject: Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, Brassica leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical Chemistry and Residue Data.

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 7/26/04

MRIDs: 45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

DP Barcode: D368042, D368086

Subject: Pyraclostrobin. Label amendment for the ultra low volume (ULV) aerial application on Corn and Wheat.

From: M. Negussie

To: T. Kish

Dated: 11/30/09

MRIDs: 47774601 and 47774602

Template Version November 2003



Pyraclostrobin /PC Code 099100/BASF Corporation.

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

Crop Field Trial – Corn Forage

Primary Evaluator	<i>Meheret Negussie</i>	03/02/2011
	Meheret Negussie, Chemist RAB3/HED (7509P)	
Approved by	<i>Leung Cheng</i>	03/16/2011
	Leung Cheng, Senior Chemist RAB3/HED (7509P)	

This DER was originally prepared under contract by Versar, Inc. (6850 Versar Center, Springfield, VA 22151; submitted 01/05/2011). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

48037315. Dyk, M. (2010) Magnitude of Pyraclostrobin Residues in Field Corn Forage Following a Single Application of BAS 500 18F in Support of Registration of BAS 500 20F. Unpublished study prepared by BASF Crop Corporation. 53 pages.

EXECUTIVE SUMMARY:

BASF Corporation has submitted crop field trial data for pyraclostrobin in/on field corn forage. Four crop trials were conducted, encompassing NAFTA Zones 11 (Idaho, one trial), 5 (North Dakota, two trials), and 1A (Prince Edward Island, one trial) during the 2009 growing season. One treated plot and one untreated control plot were established at each trial site. For each trial, one broadcast foliar application of the test substance pyraclostrobin, as an encapsulated formulation (BAS 500 18F), was made at a target rate of 0.10 lb ai/A. The actual application rate was 0.10-0.11 lb ai/A. All applications were made using ground equipment in 18 to 24.5 gal/A of water. An adjuvant (crop oil concentrate) was added to the spray mixtures for all applications. Single control and duplicate samples were collected at 7, 14, and 21 days after the last application.

Residues of pyraclostrobin and its desmethoxy metabolite (500M07) were quantitated using a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method, BASF analytical method number D9908 (Version II). The method was adequate for data collection based on acceptable concurrent method recoveries. The limit of quantitation (LOQ) was 0.02 ppm for each analyte and the limit of detection (LOD) was 0.004 ppm for each analyte.

Samples were stored frozen for a maximum of 69 days from sampling to extraction. Stability data are available indicating that both pyraclostrobin and 500M07 are stable in various crops, including wheat grain and straw, for up to 25 months in frozen storage (L. Cheng, DP# 269668, 11/28/01). By translation, these data are adequate to support the storage conditions and durations of the field corn forage samples discussed in this DER.

Following one broadcast foliar application of pyraclostrobin at a target rate of 0.10 lb ai/A, maximum total residues of pyraclostrobin (pyraclostrobin + 500M07, expressed as parent



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equivalents) in/on field corn forage were 0.63 ppm at a PHI of 7 days, 0.29 ppm at a PHI of 14 days, and 0.10 ppm at a PHI of 21 days.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 380634.

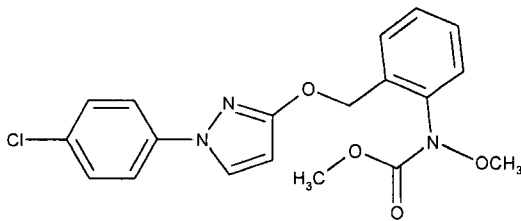
COMPLIANCE:

The study described was not conducted according to the EPA Good Laboratory Practice Standards (40 CFR Part 160), as it is a non-GLP study.

A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance that inhibits spore germination and mycelial growth and sporulation of the fungus on the leaf surface.

The chemical structure and nomenclature of pyraclostrobin and its regulated metabolite are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.

TABLE A.1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.	
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
Molecule weight	387.8
IUPAC name	methyl 2-[1-(4-chlorophenyl)pyrazol-3-yl]oxy]-N-methoxycarbamate
CAS name	methyl N-[2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]-N-methoxycarbamate
CAS registry number	175013-18-0
End-use product (EPs)	Encapsulated formulation containing pyraclostrobin as the active ingredient (250 g/L); (BAS 500 18F)



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TABLE A.1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.

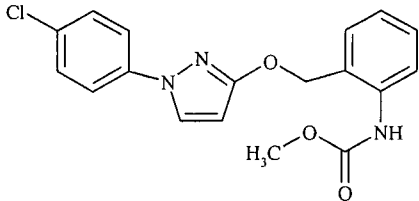
Regulated metabolite	
Common name	pyraclostrobin desmethoxy metabolite
Company experimental name	BF 500-3
Molecular weight	357.8
Chemical name	Methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl] carbamate

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.

Parameter	Value	References ¹
Melting point/range	63.7-65.2°C	D269848 & D274191
pH	Not reported	D269848 & D274191
Density	1.285 g/cm ³ at 20°C	D269848 & D274191
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)	D269848 & D274191
Solvent solubility (g/100 mL at 20°C)	acetone 16-20 ethyl acetate 6.7-8.0 methanol 4-5 2-propanol <0.01 acetonitrile 4-5 dichloromethane 20-25 toluene 2-5 n-heptane <0.01 1-octanol <0.01 olive oil 2.9 N,N-DMF >25	D269848 & D274191
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20°C 6.4 x 10 ⁻¹⁰ hPa at 25°C	D269848 & D274191
Dissociation constant, pK _a	Does not dissociate in water.	D269848 & D274191
Octanol/water partition coefficient, Log(K _{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5	D269848 & D274191
UV/visible absorption spectrum	λ _{max} = 275 nm	D269848

¹ Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and D274191, 5/3/2001, 5/15/2001, and 6/7/2001, S. Malak).

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Refer to Table B.1.1 for trial site conditions, Table B.1.2 for study use patterns, and Table B.1.3 for geographic locations of submitted and requested trials.

TABLE B.1.1 Trial Site Conditions.

City, State, Country; Year (Trial ID)	Soil characteristics			
	Type	% OM*	pH*	CEC* meq/100 g
Northwood, ND, USA; 2009 (R090432)	Loam	4.3	7.2	NR
Fargo, ND, USA; 2009 (R090433)	Loam	5	7.9	NR
Prince Edward Island, Canada; 2009 (R090434)	Sandy Loam	3.5	6.4	NR
Payette, ID, USA; 2009 (R090435)	Baldock Silt Loam	NR	NR	NR

*These parameters are optional except in cases where their value affects the use pattern for the chemical. NR = Not reported.

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Pyraclostrobin /PC Code 099100/BASF Corporation.

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

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According to the Study Report, the crops were grown under typical agricultural practices for the trial locations. Rainfall and temperature were reported to be normal during the study period; actual temperature and precipitation data were not provided. Irrigation was used to supplement as needed.

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State/Province, Country; Year; (Trial No.)	EP ¹	Application					Tank Mix/ Adjuvants ⁴
		Method; Timing	Volume GPA ² [L/ha]	Rate (lb ai/A) [kg ai/ha]	RTI ³ (days)	Total Rate (lb ai/A) [kg ai/ha]	
Northwood, ND, USA; 2009 (R090432)	BAS 500 18F	Foliar Directed (ground); V6	18 [168]	0.10 [0.11]	--	0.10 [0.11]	Prime Oil
Fargo, ND, USA; 2009 (R090433)	BAS 500 18F	Foliar Directed (ground); V8	19.6 [183]	0.10 [0.11]	--	0.10 [0.11]	Agridex
Prince Edward Island, Canada; 2009 (R090434)	BAS 500 18F	Foliar Directed (ground); V6	24.5 [230]	0.11 [0.12]	--	0.11 [0.12]	LI 700
Payette, ID, USA; 2009 (R090435)	BAS 500 18F	Foliar Directed (ground); V6	20.1 [188]	0.10 [0.11]	--	0.10 [0.11]	Pierce

¹ EP = end-use product; BAS 500 18F is an encapsulated formulation containing pyraclostrobin as the active ingredient (250 g/L).

² GPA = Volume applied, gallons per acre.

³ RTI = retreatment interval

⁴ A commercially available adjuvant (Crop oil concentrate 1% v/v) was used at each application according to the label of the adjuvant.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Field Corn		
	Submitted	Requested ¹	
		Canada	U.S.
1A	1		
5	2		
11	1		
Total	4	N/A	

¹ In response to BASF proposed waiver for the early spray encapsulated formulation, EPA/HED advised that BASF submit a waiver request for review and consideration by Chem SAC, including residue results from field corn forage (ChemSAC minutes, 2/16/2011).

B.2. Sample Handling and Preparation

At each location, a single field corn sample was taken from the untreated control plot and duplicate samples were taken from the treated plot at 7, 14, and 21 days after the last application. All samples were commercially acceptable and were collected without bias. The untreated plots were harvested before the treated plots to avoid contamination.

All samples were frozen at the field site promptly after sample collection. Samples remained in frozen storage until shipment via ACDS freezer truck or overnight courier, on dry ice, to the analytical laboratory, BASF Agricultural Research Center (Research Triangle Park, NC). Upon arrival at BASF, samples were immediately transferred to frozen storage (<-5°C) and maintained



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frozen until homogenization and analysis. All samples were homogenized to an appropriate consistency using a Stephan floor chopper and dry ice and immediately returned to frozen storage until the time of analysis.

B.3. Analytical Methodology

Samples were analyzed for residues of pyraclostrobin using BASF method D9908, Version II, with modifications. A brief description of the method was included in the submission.

Briefly, residues of pyraclostrobin were extracted with methanol:water: 2N HCl (70:25:5, v:v:v) by polytron homogenization. After extraction, samples were centrifuged and an aliquot of the supernatant was removed and cleaned up by liquid/liquid partitioning using cyclohexane and 1N HCl saturated with NaCl. An aliquot of the cyclohexane phase was taken, evaporated to dryness, and re-dissolved in a buffered methanol:water (80:20, v/v) solution for analysis by LC/MS/MS. MS/MS detection using the positive ionization mode monitored ion transitions from m/z 388→194 for pyraclostrobin, and m/z 358→164 for 500M07.

The method LOD and LOQ were 0.004 and 0.02 ppm, respectively, for residues of pyraclostrobin and 500M07 in/on field corn.

C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2. Samples were stored frozen for a maximum of 69 days prior to extraction for analysis. The extracts were analyzed within 3 days after extraction. Storage stability data are available indicating that residues of pyraclostrobin and its metabolite 500M07 are stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and root, tomatoes, and wheat grain and straw for up to 25 months (L. Cheng, DP# 269668, 11/28/01). By translation, these data are adequate to support the storage conditions and durations of the field corn forage samples discussed in this DER.

Concurrent method recovery data are presented in Table C.1. Control field corn forage samples were fortified with pyraclostrobin and 500M07 at 0.02 and 2 ppm. Concurrent method recoveries ranged from 80-110%. The method was adequate for data collection based on acceptable concurrent method recovery data. Apparent residues of pyraclostrobin and 500M07 were each below the LOQ in/on all control samples of field corn forage used for procedural recoveries. Adequate sample chromatograms and calculations were provided.

Residue data from the field trials are reported in Table C.3. A summary of the residue data for field corn forage is presented in Table C.4. Total residues of pyraclostrobin and 500M07, in parent equivalents, ranged from 0.22 to 0.63 ppm in/on field corn forage harvested at a PHI of 7 days following one foliar application of the pyraclostrobin at a targeted total rate of 0.10 lb ai/A. Total residues of pyraclostrobin and 500M07 ranged from <0.04 - 0.29 ppm in/on field corn forage harvested at a 14-day PHI, and <0.04 - 0.10 ppm in/on field corn forage harvested at a 21-day PHI.



Pyraclostrobin /PC Code 099100/BASF Corporation.

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

Crop Field Trial – Corn Forage

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin and 500M07 from Field Corn.

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean \pm Std. Dev. ¹ (%)
Pyraclostrobin				
Field Corn (Forage)	0.02	3	89, 103, 110	101 \pm 11
	2	3	89, 88, 90	89 \pm 1
500M07				
Field Corn (Forage)	0.02	2	95, 95	95
	2	2	97, 80	89

¹ Standard deviation only applicable for sample sizes of n \geq 3 samples.**TABLE C.2. Summary of Storage Conditions.**

Matrix	Storage Temperature (°C)	Actual Storage Duration ¹	Interval of Demonstrated Storage Stability ²
Field corn forage	\leq -5	38-69 days (~1-2 months)	25 months in grape juice, sugar beet tops and root, tomatoes, and wheat grain and straw

¹ From sample collection to extraction for analysis. The extracts were analyzed within 3 days after extraction.² L. Cheng, DP# 269668, 11/28/01**TABLE C.3. Residue Data from Crop Field Trials with Pyraclostrobin.**

City, State/Province, Country; Year; (Trial No.)	Zone	Crop; Variety	Commodity or Matrix	Total Rate (lb a.i./A) [kg a.i./ha]	PHI (days) ¹	Residues (ppm)		
						Pyraclostrobin	500M07 (as parent equivalents) ²	Total ³
Northwood, ND, USA; 2009 (R090432)	5	Field Corn; Not reported	Forage	0.10 [0.11]	7	0.27 ⁴	0.06	0.33
						0.31 ⁴	0.06	0.37
					14	0.03	< 0.02	< 0.05
						0.03	< 0.02	< 0.05
					21	< 0.02	< 0.02	< 0.04
						< 0.02	< 0.02	< 0.04
Fargo, ND, USA; 2009 (R090433)	5	Field Corn; Not reported	Forage	0.10 [0.11]	7	0.54 ⁴	0.09	0.63
						0.38 ⁴	0.08	0.46
					14	0.23	0.06	0.29
						0.16	0.04	0.2
					21	0.08	0.02	0.1
						0.06	0.02	0.08
Prince Edward Island, Canada; 2009 (R090434)	1A	Field Corn; Not reported	Forage	0.11 [0.12]	7	0.33	0.05	0.38
						0.18	0.04	0.22
					14	0.07	< 0.02	< 0.09
						0.09	0.02	0.11
					21	0.05	< 0.02	< 0.07
						0.06	< 0.02	< 0.08
Payette, ID, USA; 2009 (R090435)	11	Field Corn; Not reported	Forage	0.10 [0.11]	7	0.16 ⁵	0.08	0.24
						0.15 ⁵	0.08	0.23
					14	< 0.02	< 0.02	< 0.04
						0.03	< 0.02	< 0.05
					21	< 0.02	< 0.02	< 0.04
						< 0.02	< 0.02	< 0.04

¹ PHI = Pre-harvest interval.² A molecular weight conversion factor of 1.0839 was used by the Study Author to express 500M07 in parent equivalents.³ The total residues of pyraclostrobin were determined as the sum of pyraclostrobin and 500M07 expressed as parent equivalents.⁴ Average of 3 analyses.



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DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

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⁵ Average of 2 analyses.

TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyraclostrobin.									
Commodity	Total Appl. Rate lb ai/A [kg ai/ha]	PHI (days) ¹	Residue Levels (ppm)						
			N	Min.	Max.	HAFT ²	Median (STMdR)	Mean (STMR)	Std. Dev.
Pyraclostrobin									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.15	0.54	0.46	0.29	0.29	0.13
		14	8	<0.0 2	0.23	0.20	0.05	0.08	0.08
		21	8	<0.0 2	0.08	0.07	0.04	0.04	0.02
500M07									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.04	0.09	0.09	0.07	0.07	0.02
		14	8	<0.0 2	0.06	0.05	0.02	0.03	0.01
		21	8	<0.0 2	0.02	0.02	0.02	0.02	0.00
Total ³									
Field Corn Forage	0.10-0.11 [0.11-0.12]	7	8	0.22	0.63	0.55	0.35	0.36	0.14
		14	8	<0.0 4	0.29	0.25	0.07	0.11	0.09
		21	8	<0.0 4	0.10	0.09	0.06	0.06	0.02

¹ PHI = Pre-harvest interval.

² HAFT = Highest Average Field Trial value.

³ Total residues of pyraclostrobin (pyraclostrobin + 500M07), expressed as parent equivalents.

D. CONCLUSION

The submitted field trial data are adequate and reflect the use of one foliar application of the test substance, pyraclostrobin, made to field corn plants at a target rate of 0.10 lb ai/A at V6-V8 growth stage. Samples were harvested from treated and untreated plots at PHIs of 7, 14, and 21 days at all trials.

An acceptable method was used for the quantitation of residues of in/on field corn forage. Adequate storage stability data are available to support the storage conditions and durations of samples discussed in this DER. Following one broadcast foliar application of pyraclostrobin at a target rate of 0.10 lb ai/A, maximum total residues of pyraclostrobin in/on field corn forage were 0.63 ppm at a PHI of 7 days, 0.29 ppm at a PHI of 14 days, and 0.10 ppm at a PHI of 21 days.

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Pyraclostrobin /PC Code 099100/BASF Corporation.

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

Crop Field Trial – Corn Forage

E. REFERENCES

DP #s: 269668, 272771, 272789, 274095,
274192, 274471, 274957, 275843, and 278429

Subject: PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops:
Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits,
Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean),
Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root
Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits,
Strawberry, Sugar Beet, Tree Nuts, Tuberos and Corm
Vegetables, and Wheat. Review of Analytical Methods and
Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS
#175013-18-0.

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 11/28/01

MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537,
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45367501, 45399401, and 454299

F. DOCUMENT TRACKING

RDI: Meheret Negussie (03/02/2011); ChemTeam (03/09/2011); Leung Cheng (03/16/2011)

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